Chapter 10: Bonding and Molecular Structure: Orbital Hybridization and Molecular Orbitals

Molecular Orbital Theory

- MO theory assumes that pure s and p atomic orbitals of the atoms in the molecule combine to produce orbitals that are delocalized over several atoms or even an entire molecule. Those orbitals are called molecular orbitals.
- 1st principle of molecular orbital theory: the total number of molecular orbitals is always equal to the total number of atomic orbitals contributed by the atoms that have combined.
- 2nd principle of molecular orbital theory: the bonding molecular orbital is lower in energy than the parent orbitals, and the antibonding orbital is higher in energy.
- 3rd principle of molecular orbital theory: electrons of the molecule are assigned to orbitals of successively higher energy.
- Bond order = \( \frac{1}{2} (\text{number of e's in bonding MOs} - \text{number of e's in antibonding MOs}) \)
- 4th principle of MO theory: atomic orbitals combine to form molecular orbitals most effectively when the atomic orbitals are of similar energy.

Chapter 14: Solutions and Their Behavior

Molality of solute \( m = \frac{\text{amount of solute (moles)}}{\text{mass of solvent (kg)}} \)

Mole fraction: the amount of that component divided by the total amount of all of the components in the mixture.

\[
\text{Mole fraction of A (X_A)} = \frac{n_A}{(n_A + n_B + n_C + \ldots)}
\]

- The sum of the mole fractions of the components in the solutions equals 1.000. This holds true for the solute and solvent in all solutions.

Weight percent: mass of one component divided by the total mass of the mixture, multiplied by 100%.

\[
\text{Weight % of A} = \left( \frac{\text{mass of A}}{\text{mass of A + mass of B + mass of C + \ldots}} \right) \times 100\%
\]

- If you know the weight percent of a solute, you can determine its mole fraction of molality.

Parts per million (ppm) is often used to express concentration. It refers to relative amounts by mass.

- Units of ppm and mg/L are approximately equal.
- 1.0 ppm = 1.0 g of a substance in a sample with a total mass of 1.0 million g.

Liquids Dissolving in Liquids

- If 2 liquids mix to an appreciable extent to form a solution, they are said to be miscible.
- Immiscible liquids do not mix to form a solution; they exist in contact with each other as separate layers.
• “like dissolves like”
  o 2 or more nonpolar liquids or 2 or more polar liquids are both usually miscible
  o Basis of “like dissolves like”
    ▪ With H₂O and C₂H₅OH, the major force between molecules is hydrogen bonding in the –OH groups. When the 2 are mixed, hydrogen bonding between H₂O and ethanol also occurs
  o Polar and nonpolar liquids usually are not miscible

Solids Dissolving in Water
• “like dissolves like” also holds for molecular solids dissolving in liquids
• “like dissolves like” is less effective for ionic solids
  o For ionic compounds dissolving in H₂O, entropy usually favors solution

Dissolving Gases in Liquids: Henry’s Law
• Henry’s Law: the solubility of a gas in a liquid is directly proportional to the gas pressure
  \( S_g = k_H P_g \)
  \( S_g \) = gas solubility
  \( P_g \) = partial pressure of gaseous solute
  \( k_H \) = Henry’s law constant (a constant characteristic of the solute and solvent)

Temperature Effects on Solubility: Le Chatelier’s Principle
• The solubility of all gases in water decreases with increasing temperature
  o Example: bubbles appearing when you boil water
  • Le Chatelier’s principle: a change in any of the factors determining an equilibrium cases the system to adjust so as to reduce or counteract the effect of the change.
    o If a solution of a gas in a liquid is heated, the equilibrium will shift to absorb some of the added heat energy.

Changes in Vapor Pressure: Raoult’s Law
• When vapor pressure of the solvent over a solution is measured at a given temperature, it is observed that:
  o The vapor pressure of the solvent over the solution is lower than the vapor pressure of the pure solvent
  o The vapor pressure of the solvent, \( P_{solvent} \), is proportional to the relative number of solvent molecules in the solution

  \( P_{solvent} = X_{solvent} P_{solvent}^{°} \)
  \( X_{solvent} \) = molar fraction of solvent

• An ideal solution is one that obeys Raoult’s Law
• Raoult’s Law is a good approximation of solution behavior in many instances, especially at low solute concentration
• Concentrations of solute greater than 2.00 m lead to a large decrease in vapor pressure and consequently show a higher boiling point
• Solute concentrations less than 2.00 m show a smaller decrease in vapor pressure and a smaller increase in boiling point

  \( \text{Elevation in boiling point} = \Delta T_{bp} = K_{bp} m_{solute} \)
  o \( K_{bp} \) is a proportionality constant called the molal boiling point elevation constant
Units for $K_{bp}$ are in degree/molal ($^\circ\text{C}/m$)

**Freezing Point Depression**
- A consequence of dissolving a solute in a solvent is that the freezing point of the solution is lower than that of the pure solvent
- **Freezing point depression** = $\Delta T_{fp} = K_{fp}m_{\text{solute}}$
  - $K_{fp}$ values are negative so the result of the calculation is a negative value for $\Delta T_{fp}$, signifying a decrease in temperature

**Molar Mass Determination**
- Change in vapor pressure, boiling point elevation, freezing point depression, or osmotic pressure $\rightarrow$ solution concentration (use mass of solvent) $\rightarrow$ mass of solute (g solute/mol solute) $\rightarrow$ molar mass

**Colligative Properties of Solutions Containing Ions**
- Colligative properties depend not on what is dissolved but only on the number of particles of solute per solvent particle
- When 1 mol of NaCl dissolves, 2 moles of ions forms, which means the effect on the freezing point of H$_2$O should be 2x larger as that expected for a mole of sugar
- Example: A 0.100 m solution of NaCl really contains two solutes, 0.100 m Na$^+$ and 0.100 m Cl$^-$.  
  - To estimate total molality of solute particles:
    - $m_{\text{total}} = m(\text{Na}^+) + m(\text{Cl}^-) = (0.100 + 0.100) \text{ mol/kg} = 0.200 \text{ mol/kg}$
    - $\Delta T_{fp} = (-1.86 \, ^\circ\text{C}/m)(0.200 \, m) = -0.372 \, ^\circ\text{C}$
  - To estimate the freezing point depression for an ionic compound, find the molality of solute from the mass and molar mass of the compound. Then, multiply the number you get by the number of ions in the formula.
    - NaCl: $i = 2$
    - Na$_2$SO$_4$: $i = 3$
  - The ratio of the experimentally observed value of $\Delta T_{fp}$ to the value calculated, assuming no ionization, is called the van’t Hoff factor and is represented by $i$
    - $i = \frac{\Delta T_{fp, \text{measured}}}{\Delta T_{fp, \text{calculated}}} = \frac{\Delta T_{fp, \text{measured}}}{K_{fp} m}$
    - $\Delta T_{fp, \text{measured}} = K_{fp} \times m \times i$

**Osmosis**: movement of solvent molecules through a semipermeable membrane from a region of lower solute concentration to a region of higher solute concentration
- Osmotic pressure: pressure created by the column of solution for the system at equilibrium
  - A measure of this pressure is the difference in the height of the solution in the tube and the level of pure water in the beaker
- $\Pi = cRT$
  - $\Pi =$ osmotic pressure
  - $c =$ concentration
  - $T =$ temperature (K)
Colloids: represent a state intermediate between a solution and a suspension

- Colloids are different from solutions and suspensions
  - A solution is a homogeneous mixture of 2 or more substances in a single phase. In a true solution, no settling of the solute should be observed and the solute particles should be in the form of ions or relatively small molecules
  - An example of a suspension is the result of when a handful of fine sand is added to H₂O and shaken vigorously. The sand particles are still visible and gradually settle to the bottom of the beaker or bottle
- Colloid means “glue”
- Characteristics
  - Colloids usually have high molar masses (i.e. proteins)
  - Particles of a colloid are relatively large (1000 nm in diameter)
    - Because of this, they exhibit the Tyndall effect meaning the mixture appears cloudy
  - Even though colloid particles are large, they are not so large that they settle out
- Sol is used for a dispersion of a solid substance in a fluid medium
- Gel is used for a dispersion that has a structure that prevents it from being mobile

Types of Colloids
- Colloids are classified according to the state of the dispersed phase and the dispersing medium
- Colloids with H₂O as the dispersing medium can be classified as hydrophobic or hydrophilic
  - A hydrophobic colloid is one in which only weak attractive forces exist between the water and the surfaces of the colloidal particles
  - Hydrophilic colloids often have groups such as –OH and –NH₂ on their surfaces
    - Groups form strong H-bonds to water, stabilizing the colloid
- Emulsions: colloidal dispersion of one liquid in another
- Surfactants lower the surface tension of water

Chapter 15: Principles of Reactivity: Chemical Kinetics

Rate of reaction = change in concentration / change in time

Reaction Conditions and Rate
- Reactant concentrations, temperature, and pressure of catalysts affect the rate of reaction
- If the reactant is a solid, the surface area available for reaction will also affect the rate of reaction

Effect of Concentration on Reaction Rate
- Rate of reaction increases as concentration of reactant increases
- Rate of reaction = k[A]^m[B]^n for reaction aA + bB → xX
- The order of a reaction is the exponent of its concentration term in the rate expression, and the total reaction order is the sum of the exponents on all concentration terms
  - Order must be determined experimentally
Rate Constant, k
- $K$ relates rate and concentration at a given temperature
- First-order reaction: the units of $k$ are $\text{time}^{-1}$
- Second-order reaction: the units of $k$ are $\text{L/mol} \cdot \text{time}$
- Zero-order reaction: the units of $k$ are $\text{mol/L} \cdot \text{time}$

Determining a Rate Equation
- Rate equations must be determined experimentally
  - Initial rate: instantaneous reaction rate at the start of the reaction ($t=0$)

Concentration—Time Relationships: Integrated Rate Laws
- First-order reactions: $\ln([R]_t/[R]_0) = -kt$
  - $[R]_t$ is always less than $[R]_0$
- Second-order reactions: $(1/[R]_t) - (1/[R]_0) = kt$
- Zero-order reactions: $[R]_0 - [R]_t = kt$
- Each of the three previous equations can be rearranged to have the form $y = mx + b$

Half-Life and First-Order Reactions
- Half-life ($t_{1/2}$): time required for the concentration of a reactant to decrease to $\frac{1}{2}$ its initial value
  - Half-life is used primarily in first-order reactions
  - $t_{1/2} = 0.693/k$
    - Notice that half-life is independent of concentration